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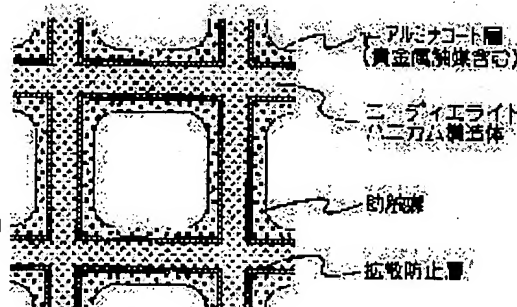
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(54) CERAMIC CARRIER AND CERAMIC CATALYST

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a ceramic carrier used in a catalyst for cleaning NO_x of a lean burn engine, low in cost, excellent in high temperature durability and capable of keeping catalytic activity over a long period of time, and to produce a ceramic catalyst.

SOLUTION: The ceramic carrier to be used is constituted by forming a diffusion preventing layer, which prevents the diffusion of an alkali metal, an alkaline earth metal, or the like, supported as an NO_x occluding material, on the surface of a cordierite honeycomb structure. The diffusion preventing layer comprises a ceramic material such as Y₂O₃, NiO, CeO₂, or the like, with a melting point of >1,000°C, not reacting with the alkali metal, the alkaline earth metal, or the like, at temperature up to 1,000°C, and, since the internal diffusion of a catalytic component such as



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CLAIMS

[Claim(s)]

[Claim 1] Ceramic support characterized by coming to form the diffusion prevention layer which prevents diffusion of the catalyst component supported in the front face of a ceramic honeycomb structure object, and for this diffusion prevention layer not reacting to it substantially with the above-mentioned catalyst component under a service temperature condition, and the melting point consisting of a high ceramic ingredient from a use maximum temperature.

[Claim 2] Ceramic support according to claim 1 whose coefficient of thermal expansion of the direction of passage is less than $[1.5 \times 10^{-6} / \text{degree C}]$.

[Claim 3] Ceramic support according to claim 1 or 2 whose melting point of the ceramic ingredient which constitutes the above-mentioned diffusion prevention layer is 1000 degrees C or more.

[Claim 4] 3 is [claim 1 which the above-mentioned ceramic honeycomb structure object becomes from the ingredient which has reactivity to the above-mentioned catalyst component thru/or] the ceramic support of a publication either.

[Claim 5] Ceramic support according to claim 4 which the above-mentioned ceramic honeycomb structure object turns into from the ceramic ingredient containing Si.

[Claim 6] Ceramic support according to claim 5 whose above-mentioned ceramic honeycomb structure object is cordierite.

[Claim 7] 6 is [claim 1 in which the above-mentioned catalyst component contains at least one sort chosen from alkali metal and alkaline earth metal thru/or] the ceramic support of a publication either.

[Claim 8] Ceramic support according to claim 7 in which the above-mentioned catalyst component contains a potassium.

[Claim 9] 8 is [claim 1 whose porosity of the above-mentioned diffusion prevention layer is 50% or less thru/or] the ceramic support of a publication either.

[Claim 10] 9 is [claim 1 which the ceramic ingredient which constitutes the above-mentioned diffusion prevention layer becomes from aluminas other than alpha mold, nickel, Cu, Zn and Y, and the metallic oxide containing at least one sort chosen from a lanthanoids thru/or] the ceramic support of a publication either.

[Claim 11] 10 is [claim 1 whose thickness of the above-mentioned diffusion prevention layer is below the average pole diameter of the above-mentioned ceramic honeycomb structure object thru/or] the ceramic support of a publication either.

[Claim 12] For the above-mentioned diffusion prevention layer, 11 is [claim 1 currently formed with a dip method PVD, or a CVD method thru/or] the ceramic support of a publication either.

[Claim 13] 12 is [claim 1 in which it is formed in with a dip method, and the above-mentioned diffusion prevention layer repeats a series of processes dried / are immersed and / and calcinated in DIP liquid two or more times, and is formed thru/or] the ceramic support of a publication either.

[Claim 14] 13 is [claim 1 by which the above-mentioned diffusion prevention layer is formed in water solubility or a nonaqueous solubility solvent with the dip method using the slurry which carried out homogeneity distribution of the particle of the above-mentioned ceramic ingredient as DIP liquid thru/or] the ceramic support of a publication either.

[Claim 15] For the above-mentioned diffusion prevention layer, 13 is [claim 1 by which the raw material of the above-mentioned ceramic ingredient is formed in water solubility or a nonaqueous solubility solvent with the dip method using the solution which exists in homogeneity by the ionic state

as DIP liquid thru/or] the ceramic support of a publication either.

[Claim 16] 15 is [claim 1 which comes to form the interlayer which it has a different coefficient of thermal expansion from these, and the melting point becomes from a high ceramic ingredient from a use maximum temperature between the above-mentioned ceramic honeycomb structure object and the above-mentioned diffusion prevention layer at least one thru/or more than it thru/or] the ceramic support of a publication either.

[Claim 17] Ceramic support according to claim 16 whose thickness of the above-mentioned above-mentioned interlayer is below the average pole diameter of the above-mentioned ceramic honeycomb structure object.

[Claim 18] Ceramic support according to claim 16 or 17 in which the above-mentioned middle class is formed with a dip method, PVD, or a CVD method.

[Claim 19] 18 is [claim 16 in which it is formed in with a dip method, and the above-mentioned middle class repeats a series of processes dried / are immersed and / and calcinated in DIP liquid two or more times, and is formed thru/or] the ceramic support of a publication either.

[Claim 20] 19 is [claim 16 by which the above-mentioned interlayer is formed in water solubility or a nonaqueous solubility solvent with the dip method using the slurry which carried out homogeneity distribution of the particle of the above-mentioned ceramic ingredient as DIP liquid thru/or] the ceramic support of a publication either.

[Claim 21] For the above-mentioned interlayer, 19 is [claim 16 by which the raw material of the above-mentioned ceramic ingredient is formed in water solubility or a nonaqueous solubility solvent with the dip method using the solution which exists in homogeneity by the ionic state as DIP liquid thru/or] the ceramic support of a publication either.

[Claim 22] 21 is [claim 1 whose mean particle diameter of the primary particle of the ceramic particle which constitutes either / at least / the above-mentioned diffusion prevention layer or the above-mentioned interlayer is below an average pole diameter of the above-mentioned ceramic honeycomb structure object thru/or] the ceramic support of a publication either.

[Claim 23] Ceramic support according to claim 22 whose mean particle diameter of the primary particle of the ceramic particle which constitutes either [at least] the above-mentioned diffusion prevention layer or the above-mentioned interlayer is 1/10 or less [of the average pole diameter of the above-mentioned ceramic honeycomb structure object].

[Claim 24] 23 is [claim 16 which is the mixture thru/or the conjugated compound of a ceramic ingredient which constitutes the ceramic ingredient with which the ceramic ingredients which constitute the above-mentioned interlayer differ in the ceramic ingredient which constitutes the above-mentioned ceramic honeycomb structure object and the above-mentioned diffusion prevention layer, crystal form, an anisotropy and a configuration element, or a compound presentation or the above-mentioned ceramic honeycomb structure object, and the above-mentioned diffusion prevention layer thru/or] the ceramic support of a publication either.

[Claim 25] 24 is [above-mentioned claim 1 thru/or] the ceramic catalyst object characterized by coming to form the catalyst component support layer containing the above-mentioned catalyst component in the front face of the ceramic support of a publication either.

[Claim 26] It is the ceramic catalyst object according to claim 25 with which the above-mentioned diffusion prevention layer does not react to the bottom of a service-temperature condition substantially with a potassium, and the melting point consists of a high ceramic ingredient from a use maximum temperature by the above-mentioned catalyst component supported by the above-mentioned catalyst component support layer consisting of a diffusion prevention layer in which the above-mentioned ceramic support is formed in a ceramic honeycomb structure object and its front face, and prevents diffusion of a potassium including a potassium at least.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the catalyst for emission gas purification which purifies the exhaust gas from internal combustion engines, such as an automobile engine, the detailed ceramic support optimal as support of the catalyst for emission gas purification of a lean burn engine or a diesel power plant, and the ceramic catalyst object using this.

[0002]

[Description of the Prior Art] The so-called three way component catalyst which purifies conventionally CO, HC, and NO_x which are discharged from an automobile to coincidence is used widely. It is cleaning and CO₂ of the further exhaust gas because of protection of recent years and natural environment. Reduction of a discharge is demanded and the lean combustion (lean burn) method which can reduce the amount of exhaust gases by the improvement in fuel consumption is adopted widely. However, in order for the conventional three way component catalyst to be unable to demonstrate an original function but to compensate this with it from the NO_x purification engine performance falling by the Lean side (hyperoxia ambient atmosphere), the catalyst for emission gas purification of an NO_x occlusion reduction type is developed. precious metal catalysts, such as Pt, Rh, etc. by which this is used for the usual three way component catalyst, -- in addition, in lean atmosphere, it comes to add the NO_x occlusion material which emits and purifies NO_x by which carried out occlusion of NO_x and occlusion was carried out in SUTOIKI (theoretical air fuel ratio) thru/or a rich ambient atmosphere as a co-catalyst, and alkaline earth metal, such as basic alkali metal, such as Na, strong K, strong Cs, etc., and Mg, Sr, Ba, is used for NO_x occlusion material.

[0003] The catalyst for emission gas purification of an NO_x occlusion reduction type has a publication in JP,6-31139,A, the coat of the porous bodies, such as gamma-alumina, is carried out to the honeycomb support which consists of ceramics, such as cordierite which is excellent in thermal resistance with a low-thermal expansion ingredient, and it is indicated by the catalyst which made an alkali-metal oxide and Pt support that reduction of the NO_x discharge in the Lean condition is possible. However, since HC purification engine performance will fall if the basicity of the alkali metal which is NO_x occlusion material is too strong, NO_x occlusion material has been chosen to compensate for the engine performance made into the purpose.

[0004] On the other hand, exhaust gas temperature has elevated-temperature-ized in recent years, and improvement in the elevated-temperature endurance of the catalyst for emission gas purification is important in connection with this. However, the catalyst which supported alkali metal as NO_x occlusion material to cordierite support had the problem which causes the fall of NO_x occlusion ability, and degradation of cordierite support, when exhaust gas temperature became high. This has proposed using the support which it becomes that alkali metal passes through the inside of the coat layer which consists of porous gamma-alumina etc. easily, and reacts with Si in cordierite from the low-thermal expansion ingredient which is considered to be the cause, replaces with cordierite support as the cure in JP,10-165817,A, and does not contain Si.

[0005] However, only aluminum titanate with a very big (heavy) consistency shows a coefficient of thermal expansion low practically enough among alpha-alumina illustrated by JP,10-165817,A, a zirconia, a titania, phosphoric-acid titanium, aluminum titanate, stainless steel, and a Fe-aluminum-Cr

alloy. That is, metal support has the problem that a price is high, the top where aluminum titanate is disadvantageous in respect of the formation of car lightweight. Its coefficient of thermal expansion is large, and if other ceramic ingredients take thermal shock resistance into consideration, they are not practical. Thus, the actual condition is that the cheap support ingredient is not obtained in the low-thermal expansion coefficient replaced with cordierite.

[0006] The emission-gas-purification filter which prepared upwards the coating layer which consists or more of at least one of a silica, a zirconia, a titania, and the silica aluminas on ceramic support, and supported alkali metal and an alkaline earth metal is indicated by JP,10-137590,A, and it is indicated that diffusion inside [of a catalyst component] a filter is controlled by the coating layer. However, it became clear that the ingredient of these coatings layer reacted with alkali metal and alkaline earth metal in about 800-degree C conditions which are the service temperature of the catalyst for emission gas purification, and a compound was generated as a result of this invention person's examination. That is, they are able for alkali metal and an alkaline earth metal to react with a coating layer, and for an excessive alkali metal and an alkaline earth metal to diffuse the interior, to arrive at a filter front face, and to react with this further, in a high temperature service 800 degrees C or more. Therefore, it was difficult to suppress diffusion of alkali metal and alkaline earth metal by the coating layer which consists of these ingredients in the present condition that the maximum temperature of exhaust gas rises to near 1000 degree C.

[0007]

[Problem(s) to be Solved by the Invention] This invention is cheap, is excellent in elevated-temperature endurance, moreover, reacts with the alkali metal as NO_x occlusion material supported as a co-catalyst, and an alkaline earth metal, does not reduce the catalyst engine performance, is used for the catalyst for emission gas purification of a lean burn engine, and aims at realizing the ceramic support and the ceramic catalyst object which can maintain the required catalyst engine performance over a long period of time.

[0008]

[Means for Solving the Problem] Invention of claim 1 of this invention is ceramic support which comes to form the diffusion prevention layer which prevents diffusion of the catalyst component supported in the front face of a ceramic honeycomb structure object, does not react with the above-mentioned catalyst component substantially under a service temperature condition, and constitutes this diffusion prevention layer from a ceramic ingredient with the melting point higher than a use maximum temperature.

[0009] Since the above-mentioned diffusion prevention layer does not react substantially with the above-mentioned catalyst component in the service temperature of a catalyst, the above-mentioned catalyst component does not diffuse it inside the above-mentioned diffusion prevention layer. Therefore, it can prevent that the diffused above-mentioned catalyst component arrives at the front face of the above-mentioned ceramic honeycomb structure object, and reacts with this. Moreover, since the above-mentioned diffusion prevention layer has the melting point higher than the use maximum temperature of a catalyst, the diffusion prevention effectiveness does not fall by melting. For this reason, it is possible to constitute the above-mentioned ceramic honeycomb structure object from cordierite which is cheap and is excellent in elevated-temperature endurance, and since the catalyst engine performance is moreover maintainable over a long period of time, it is the optimal as a catalyst for emission gas purification of a lean burn engine.

[0010] In invention of claim 2, the coefficient of thermal expansion of the direction of passage makes the above-mentioned ceramic support the following [$1.5 \times 10^{-6} / \text{degree C}$]. Even if it uses it for the catalyst for emission gas purification into which thermal shock resistance improves and hot exhaust gas flows by this, fear of thermal shock destruction is small.

[0011] In invention of claim 3, the melting point of the ceramic ingredient which constitutes the above-mentioned diffusion prevention layer is made into 1000 degrees C or more. Since a maximum temperature does not exceed 1000 degrees C when using for the catalyst for emission gas purification, if the melting point is a ceramic ingredient 1000 degrees C or more, the above-mentioned diffusion prevention layer will fuse and a function will not be reduced.

[0012] In invention of claim 4, it considers as the ceramic ingredient containing Si like invention of the ingredient 5 which has reactivity for the above-mentioned ceramic honeycomb structure object to the above-mentioned catalyst component, for example, a claim. Since the ceramic ingredient containing Si

tends to react with catalyst components, such as NO_x occlusion material, it can prevent degradation by the reaction by preparing the above-mentioned diffusion prevention layer in such a case. Like invention of claim 6, as the above-mentioned ceramic honeycomb structure object, when cordierite with a low coefficient of thermal expansion is used, specifically, cost reduction and the improvement effectiveness of thermal shock resistance are high [it is cheap, and].

[0013] In invention of claim 7, the above-mentioned catalyst component contains at least one sort chosen from alkali metal and alkaline earth metal. It is used as NO_x occlusion material in the catalyst for emission gas purification, and like invention of claim 8, a potassium is suitable for these metals as the above-mentioned catalyst component, and, specifically, its NO_x occlusion effectiveness is high. However, there is concern of the degradation by diffusion inside support, and diffusion can be effectively prevented by using the ceramic support which prepared the diffusion prevention layer of this invention.

[0014] In invention of claim 9, the porosity of the above-mentioned diffusion prevention layer is made into 50% or less. porosity forms 50% or less of layer as the above-mentioned diffusion prevention layer -- the bottom of anticipated-use conditions -- the above-mentioned ceramic honeycomb structure -- it becomes possible to control diffusion, without passing a catalyst component to the inside of the body.

[0015] In invention of claim 10, it considers as the metallic oxide containing at least one sort chosen from aluminas other than alpha mold, nickel, Cu, Zn and Y, and a lanthanoids in the ceramic ingredient which constitutes the above-mentioned diffusion prevention layer. The melting point is 1000 degrees C or more, and since these ceramic ingredient does not react with the above-mentioned catalyst component of claim 7, it can prevent the diffusion certainly and can maintain the catalyst engine performance.

[0016] In invention of claim 11, thickness of the above-mentioned diffusion prevention layer is made below into the average pole diameter of the above-mentioned ceramic honeycomb structure object. Although adhesion with coat layers, such as gamma-alumina which the pore of a honeycomb structure object is buried and is formed on a diffusion prevention layer, will tend to worsen if larger than the value of an average pole diameter, this can be prevented by forming more thinly than an average pole diameter.

[0017] In claim 12, the above-mentioned diffusion prevention layer is formed with a dip method, PVD, or a CVD method. By any [these] approach, the above-mentioned diffusion prevention layer can be formed in the front face of the above-mentioned ceramic honeycomb structure object good, and diffusion of a catalyst component can be prevented.

[0018] In claim 13, the above-mentioned diffusion prevention layer is formed with a dip method, and a series of processes dried [are immersed and] and calcinated in DIP liquid in that case are repeated two or more times, and are formed. Since it is made to decrease and the above-mentioned diffusion prevention layer of high quality with few cracks can be formed in a front face by repeating the immersion to DIP liquid, desiccation, and baking for the very small crack generated in the process which is immersed in DIP liquid, dries and is calcinated further, it is high in the effectiveness of preventing a catalyst component being spread in the honeycomb structure under a service condition.

[0019] In claim 14, the above-mentioned diffusion prevention layer is formed in water solubility or a nonaqueous solubility solvent with the dip method using the slurry which carried out homogeneity distribution of the particle of the above-mentioned ceramic ingredient as DIP liquid. A ceramic particle is immersed into the DIP liquid preferably distributed in the state of the primary particle to homogeneity, and controls generating of the non-covered part by condensation of ceramic particles, the crack initiation by the ununiformity of thickness, etc. at the time of desiccation and baking, and the effectiveness of preventing a catalyst component being spread in the honeycomb structure under a service condition is heightened.

[0020] In claim 15, the raw material of the above-mentioned ceramic ingredient forms the above-mentioned diffusion prevention layer in water solubility or a nonaqueous solubility solvent with the dip method using the solution which exists in homogeneity by the ionic state as DIP liquid. It is made to be immersed into the DIP liquid which made the metallic element used as the above-mentioned ceramic ingredient exist in homogeneity by the ionic state, and by processing in an after that predetermined gas ambient atmosphere, DIP liquid can be made to be able to permeate to the details of the above-mentioned ceramic honeycomb structure object, the above-mentioned diffusion prevention layer without a non-covered part can be formed, and the diffusion prevention effectiveness of a catalyst component

can be heightened.

[0021] In invention of claim 16, the interlayer which it has a different coefficient of thermal expansion from these, and the melting point becomes from a high ceramic ingredient from a use maximum temperature is formed at least one thru/or more than it between the above-mentioned ceramic honeycomb structure object and the above-mentioned diffusion prevention layer.

[0022] the above-mentioned interlayer -- the service-temperature conditions of the bottom of the formation temperature condition of the above-mentioned diffusion prevention layer, or a catalyst -- the stress or the crack which generates in the above-mentioned diffusion prevention layer according to a coefficient-of-thermal-expansion difference with the above-mentioned ceramic honeycomb structure object at the time of a lower temperature hysteresis load -- decreasing -- ceramic honeycomb structure -- it becomes possible to demonstrate enough the above-mentioned effectiveness of a diffusion prevention layer prevent diffusion of the catalyst component to the inside of the body. Moreover, since the melting point is higher than the use maximum temperature of a catalyst, as for the above-mentioned interlayer, the diffusion prevention effectiveness does not fall by melting.

[0023] In claim 17, thickness of the above-mentioned diffusion prevention layer and the above-mentioned interlayer is made below into the value of the average pole diameter of the above-mentioned ceramic honeycomb structure object. It can prevent that the pore of a honeycomb structure object is buried with making it smaller than the value of an average pole diameter by formation of the above-mentioned diffusion prevention layer and the above-mentioned interlayer, and adhesion with coat layers, such as gamma-alumina on the above-mentioned diffusion prevention layer, falls.

[0024] In claim 18, the above-mentioned middle class is formed with a dip method, PVD, or a CVD method. By any [these] approach, the above-mentioned interlayer can be formed in the front face of the above-mentioned ceramic honeycomb structure object good, and the diffusion prevention effectiveness of the catalyst component by the above-mentioned diffusion prevention layer can be heightened.

[0025] In claim 19, a series of processes which form a dip method, are immersed in DIP liquid in that case, dry the above-mentioned middle class, and are calcinated are repeated two or more times, and are formed. The above-mentioned interlayer of high quality with few cracks can be obtained on a front face like above-mentioned claim 13 by this, the above-mentioned diffusion prevention layer can be formed good on it, and diffusion of a catalyst component can be prevented effectively.

[0026] In claim 20, the above-mentioned interlayer is formed in water solubility or a nonaqueous solubility solvent with the dip method using the slurry which carried out homogeneity distribution of the particle of the above-mentioned ceramic ingredient as DIP liquid. The above-mentioned interlayer of the high quality which has neither a non-covered part nor a crack like above-mentioned claim 14 by this can be obtained, the above-mentioned diffusion prevention layer can be formed good on it, and diffusion of a catalyst component can be prevented effectively.

[0027] In claim 21, the raw material of the above-mentioned ceramic ingredient forms the above-mentioned interlayer in water solubility or a nonaqueous solubility solvent with the dip method using the solution which exists in homogeneity by the ionic state as DIP liquid. The above-mentioned interlayer of the high quality which has neither a non-covered part nor a crack like above-mentioned claim 15 by this can be obtained, the above-mentioned diffusion prevention layer can be formed good on it, and diffusion of a catalyst component can be prevented effectively.

[0028] In claim 22, mean particle diameter of the primary particle of the ceramic particle which constitutes either [at least] the above-mentioned diffusion prevention layer or the above-mentioned interlayer is made below into the average pole diameter of the above-mentioned ceramic honeycomb structure object. The effectiveness of being making mean particle diameter of the primary particle of the above-mentioned ceramic particle or less [of the average pole diameter of the above-mentioned ceramic honeycomb structure object] into 1/10 like claim 23, and preventing preferably formation to homogeneity being attained also on the pore front face of the above-mentioned ceramic honeycomb structure object, and a catalyst component diffusing the above-mentioned diffusion prevention layer or the above-mentioned interlayer in the honeycomb structure under a service condition is heightened.

[0029] Like claim 24, even if the ceramic ingredient which constitutes the above-mentioned interlayer is a different ceramic ingredient in the ceramic ingredient which constitutes the above-mentioned ceramic honeycomb structure object and the above-mentioned diffusion prevention layer, crystal form, an anisotropy and a configuration element, or a compound presentation, it may be the mixture thru/or the

conjugated compound of a ceramic ingredient which constitutes the above-mentioned ceramic honeycomb structure object and the above-mentioned diffusion prevention layer. By all, the above-mentioned diffusion prevention layer can be formed good on it, and diffusion into the honeycomb structure of a catalyst component can be prevented.

[0030] claim 25 -- invention of a ceramic catalyst object -- it is -- above-mentioned claim 1 thru/or either of 24 -- come to form the catalyst component support layer containing the above-mentioned catalyst component in the front face of the ceramic support of a publication, for example, form coat layers, such as gamma-alumina, in the ceramic support of this invention, a catalyst is made to support, and it is obtained. Suitably, the above-mentioned ceramic support consists of a diffusion prevention layer which the above-mentioned catalyst component supported by the above-mentioned catalyst component support layer is formed in a ceramic honeycomb structure object and its front face, including a potassium at least, and prevents diffusion of a potassium like invention of claim 26. By not reacting to the bottom of a service temperature condition substantially with a potassium, and constituting this diffusion prevention layer from a ceramic ingredient with the melting point higher than a use maximum temperature, it can prevent that a potassium is spread inside the above-mentioned ceramic support, and can be compatible in improvement in cost reduction and the catalyst engine performance.

[0031]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The ceramic support of this invention consists of a ceramic honeycomb structure object which consists of ceramic ingredients, such as cordierite, and a diffusion prevention layer which is formed in the front face and prevents diffusion of the catalyst component supported, as shown in drawing 1. Moreover, if needed, as shown in drawing 2, the interlayer of a different coefficient of thermal expansion from these can also be formed between a ceramic honeycomb structure object and a diffusion prevention layer. The ceramic catalyst object which the coat layer which consists of gamma-alumina etc. was formed [object] in the front face of such ceramic support of a configuration as a catalyst support layer containing a catalyst component, and made it support a catalyst is suitable as an internal combustion engine, for example, a catalyst for emission gas purification of a lean burn engine. In addition to precious metal catalysts, such as Pt, co-catalysts, such as NOx occlusion material, are usually used for the catalyst in this case. The barium and the potassium which are excellent in NOx occlusion ability are preferably used suitably including at least one sort of metals with which NOx occlusion material is chosen from alkaline earth metal, such as alkali metal, such as Na, K, and Cs, and Mg, Sr, Ba, as a catalyst component.

[0032] Cordierite is 2MgO , $2\text{aluminum}_2\text{O}_3$, and 5SiO_2 . It is the oxide expressed with a chemical formula. It is a low-fever expansion ingredient, and since thermal resistance of cordierite is good, it is common as catalyst support. For this reason, when used as ceramic support which prepared the diffusion prevention layer in the front face, the coefficient of thermal expansion of the direction of passage is kept sufficiently low, and the thermal shock resistance at the time of elevated-temperature use is raised. However, with the catalyst for emission gas purification of an NOx occlusion mold, it is easy to react with the alkali metal in a co-catalyst, and an alkaline earth metal, and it is checked that the reason is in Si in cordierite. Not only Si but when the ceramic ingredient which has a catalyst component and reactivity is used, and also when [when the ceramic ingredient containing Si other than cordierite, for example, SiC, Si_3N_4 , a mullite, etc. are used as a ceramic honeycomb structure object ingredient or], the same problem arises.

[0033] So, in this invention, it faces using the ceramic honeycomb structure object which has catalyst components, such as cordierite, and reactivity as ceramic support, and the reaction of catalyst components, such as NOx occlusion material, and a ceramic honeycomb structure object is prevented by preparing a diffusion prevention layer in the front face. A diffusion prevention layer consists of ceramic ingredients with the melting point higher than a use maximum temperature low [the catalyst component and reactivity which are going to prevent diffusion of NOx occlusion material etc. under a service temperature condition]. What is necessary is not to react with catalyst components, such as alkali metal and alkaline earth metal, below 1000 degrees C, but just to use the ceramic ingredient which has the melting point of 1000 degrees C or more, since it usually goes up to near 1000 degrees C of maximum temperatures at about 800 degrees C whenever [catalyst temperature / at the time of use] in the case of the catalyst for emission gas purification. Since a diffusion prevention layer fuses that the melting point is less than 1000 degrees C by the use maximum temperature, the diffusion prevention effectiveness

falls.

[0034] as the example of the ceramic ingredient which constitutes a diffusion prevention layer -- gamma-aluminum $2O_3$ etc. -- the metallic oxide containing at least one sort chosen from lanthanoids, such as aluminas other than alpha mold, nickel, Cu, Zn and Y, and La, Ce, Er, Yb, is mentioned. Since these metallic oxides are ingredients with low reactivity with the alkali metal as NO_x occlusion material, and alkaline earth metal, they limit a catalyst component to a ceramic carrier surface, and can prevent diffusion inside. In order to acquire this effectiveness, the lower possible one of the porosity of a diffusion prevention layer is good, and it is desirable that porosity is 50% or less suitably.

[0035] Since it can become the diffusion path of a catalyst component when the crack which leads to a front face from a ceramic honeycomb structure object exists here, as a diffusion prevention layer, it is desirable that there are few cracks. Compared with a low-fever expansion ingredient like cordierite, generally other ceramic ingredients have a large coefficient of thermal expansion, and the ceramic ingredient which constitutes the above-mentioned diffusion prevention layer is not an exception, either. For this reason, if the above-mentioned diffusion prevention layer is constituted from a ceramic ingredient with a larger coefficient of thermal expansion than the cordierite used as a ceramic honeycomb structure object, when forming the time of elevated-temperature use, or a diffusion prevention layer under an elevated temperature, it exfoliates in a differential thermal expansion, or both a diffusion prevention layer, and ceramic honeycomb structure both [either or] have a possibility that a crack may arise. Since a diffusion prevention layer is formed thinly enough compared with a honeycomb structure object, the thermal stress to generate becomes large according to the temperature gradient which is easy to produce distortion to the stress produced according to heat deformation, and is produced within and without a diffusion prevention layer in the differential thermal expansion of a diffusion prevention layer and a honeycomb structure object, and it becomes easy to produce a crack.

[0036] Then, in such a case, the interlayer who consists of a ceramic ingredient of a different coefficient of thermal expansion from these is formed at least one thru/or more than it between a ceramic honeycomb structure object and a diffusion prevention layer. This interlayer is also good for a ceramic ingredient with the melting point higher than a use maximum temperature and the ceramic ingredient which has the melting point of 1000 degrees C or more preferably to constitute from the same reason as a diffusion prevention layer.

[0037] When a coefficient of thermal expansion constitutes an interlayer from a ceramic ingredient between a honeycomb structure object and a diffusion prevention layer, when it constitutes on the other hand from a ceramic ingredient with a larger coefficient of thermal expansion than a diffusion prevention layer, it acts as a sacrifice layer of the stress produced in a diffusion prevention layer, and the effectiveness that neither produces the diffusion path of a catalyst component as a crack does not arise in a diffusion prevention layer is acquired as a buffer coat of thermal expansion. However, since there is a possibility of the bond strength of a honeycomb structure object, an interlayer, and a diffusion prevention layer falling, and producing exfoliation in using as a sacrifice layer, it is good to constitute as a buffer coat preferably.

[0038] You may be the ingredient which combined the ceramic ingredient which constitutes a honeycomb structure object and a diffusion prevention layer also with a ceramic ingredient which is different as a ceramic ingredient which constitutes an interlayer in the ceramic ingredient which constitutes a ceramic honeycomb structure object and a diffusion prevention layer, crystal form, an anisotropy and a configuration element, or a compound presentation, for example, a mixolimnion and a conjugated compound layer. Or a two or more layers interlayer may be formed, a component may be changed gradually, and the effectiveness which controls the crack of a diffusion prevention layer is acquired using the difference in a coefficient of thermal expansion. In any case, the direction which selects the ceramic ingredient near the coefficient of thermal expansion of a honeycomb structure object and a diffusion prevention layer is advantageous to control of the crack by the differential thermal expansion.

[0039] as the example of the ceramic ingredient which constitutes an interlayer -- aluminum $2TiO_5$, ZnO, Y_2O_3 , AlN, and TiO_2 etc. -- it is mentioned. in addition, alpha-aluminum $2O_3$, gamma-aluminum $2O_3$, ZrO_2 , CeO_2 , NiO, CuO, MgO and La $2O_3$, and Er $2O_3$ etc. -- non-oxides (a compound non-oxide is also good), such as an oxide (a multiple oxide is also good), and carbide, a nitride, are also usable, and if it is the ceramic ingredient with which coefficients of thermal expansion differ, according

to a coefficient of thermal expansion, an ingredient can be chosen as a buffer coat or a sacrifice layer. The general coefficient of thermal expansion of each ceramic ingredient is indicated by various ceramic ingredient-related reference etc. (for example, reference, such as the Ceramic Society of Japan edit "the mechanical property of the ceramics", and "knowledge of an ingredient").

[0040] How to manufacture the ceramic support of the above-mentioned configuration is explained. When a ceramic honeycomb structure object consists of cordierite, as a cordierite-ized raw material, oxide, such as talc, a kaolin, and an alumina, is used, generally, these cordierite-ized raw material is prepared so that it may become the above-mentioned theoretical presentation, and a honeycomb Plastic solid is acquired by adding, kneading and carrying out extrusion molding of shaping assistants, such as a binder, lubricant, and a moisturizer, and the water. After heating this Plastic solid in atmospheric air and degreasing, it calcinates and considers as a honeycomb structure object.

[0041] The dip method immersed in the DIP liquid which contains the ceramic ingredient which constitutes a diffusion prevention layer or an interlayer as an approach of forming a diffusion prevention layer and an interlayer in the front face of this ceramic honeycomb structure object in a ceramic honeycomb structure object can be used. Preparation of DIP liquid is good by any approaches, such as an approach of obtaining the DIP liquid containing the ceramic ingredient made into the purpose by hydrolyzing the method of making a solvent distributing the particle of a desired ceramic ingredient, or a metal alkoxide as a start raw material etc., or its precursor. Then, a diffusion prevention layer can be formed by drying and calcinating by the usual approach. Or it is easy to be natural even if it forms a diffusion prevention layer using well-known thin film coating technology, such as PVD, such as a spatter and vacuum evaporation, or a CVD method using organic metal gas.

[0042] The approach of repeating a series of processes of the immersion to DIP liquid, desiccation, and baking two or more times as an approach of forming little diffusion prevention layer and middle class of a crack using a dip method is employable. Former immersion, desiccation, and the very small crack generated in process of baking can be closed by this, and the crack which leads to a front face can be abolished. Generally, the solvent used for DIP liquid is divided roughly into water solubility or a nonaqueous solubility solvent, and the DIP liquid which made homogeneity distribute a ceramic particle or its raw material in these solvents is used for it. Preferably, without making a ceramic particle condense, it is good to use the DIP liquid currently distributed by homogeneity in the state of the primary particle, and it can form a diffusion prevention layer and an interlayer in the front face of a honeycomb structure object by the thickness of the request to homogeneity by a honeycomb structure object being immersed in this DIP liquid.

[0043] Here, as for the ceramic particle which forms a diffusion prevention layer and an interlayer, it is desirable that the mean particle diameter of a primary particle is below an average pole diameter of a ceramic honeycomb structure object, and a diffusion prevention layer and an interlayer can be formed in a pore internal surface at homogeneity. In order to agree in the shape of [on the front face of pore] toothing and to form a diffusion prevention layer and an interlayer in homogeneity, it is more desirable in it being $1/10$ or less [of an average pole diameter]. As for the thickness of a diffusion prevention layer and an interlayer, it is desirable that it is below the value of the average pole diameter of a ceramic honeycomb structure object. The thickness of a diffusion prevention layer and an interlayer influences the bond strength when carrying out the coat of the coat layers, such as gamma-alumina, if the thickness of a diffusion prevention layer and an interlayer is larger than the value of an average pole diameter, the pore of a ceramic honeycomb structure object will be fill uped with a diffusion prevention layer and an interlayer, and the anchor effect of it will be lost, it will be inferior in the adhesive strength of the coat layer which carries out a coat later, and the problem which exfoliates in a differential thermal expansion will produce it. For example, since an average pole diameter is usually about 5 micrometers in the case of cordierite, the thickness of a diffusion prevention layer and an interlayer should just be less than [about 5 micrometers thru/or it]. Moreover, the mean particle diameter of the primary particle of a diffusion prevention layer and an interlayer should just be less than [about 0.5 micrometers thru/or it].

[0044] furthermore, as an approach of forming a diffusion prevention layer and an interlayer in pore smaller than submicron one or that not more than it, or the front face of a crack It considers as the solution which made the raw material of the ceramic ingredient which constitutes a diffusion prevention layer and an interlayer for DIP liquid in water solubility or a nonaqueous solubility solvent exist in homogeneity by the ionic state. After a honeycomb structure object is enough immersed in this DIP

liquid, the approach of performing processing sufficient in the bottom of a predetermined gas ambient atmosphere is employable. For example, what is necessary is just to heat-treat by nitrogen-gas-atmosphere mind by the oxidizing atmosphere, using the DIP liquid containing the metal component ion of a ceramic ingredient, if it is a nitride if it is an oxide. Since according to this approach DIP liquid is made to permeate to the pore of a honeycomb structure object, or the details of a crack and a diffusion prevention layer or the above-mentioned interlayer can be formed in that front face, the diffusion path of a catalyst component in which it is well-informed about an internal honeycomb structure object from a diffusion prevention layer can be intercepted.

[0045] On the front face of the ceramic support which has the diffusion prevention layer manufactured by the above approach, by well-known approaches, such as a dip method, the coat layer which consists of gamma-alumina etc. is formed, and a ceramic catalyst object is acquired by making a catalyst support. Co-catalysts, such as precious metal catalysts, such as Pt, and NO_x occlusion material, may be made to support by immersed and drying in the solution containing a catalyst component after carrying out the coat of the gamma-alumina to ceramic support, even if it makes it distribute in the slurry containing gamma-alumina and makes formation and coincidence of a coat layer support.

[0046] Thus, the ceramic support which has the diffusion prevention layer obtained has enough the coefficient of thermal expansion of the direction of passage as small as less than $[1.5 \times 10^{-6}/\text{degree C}]$, and its a possibility which ceramic support destroys by the thermal shock at the time of elevated-temperature use that it might say is very small. Therefore, the ceramic catalyst object which formed the catalyst support layer in this ceramic support is suitably used as a catalyst for automobile exhaust purification of for example, a lean burn system, and is compatible in thermal shock resistance and the catalyst engine performance. Conventionally without a diffusion prevention layer, with a configuration, since diffusion of catalyst components, such as NO_x occlusion material, begins from about 600 degrees C, by the operating environment by which a maximum temperature rises to about 1000 degrees C, degradation of the support by the reaction with the catalyst performance degradation by diffusion of a catalyst component and a catalyst component etc. poses a problem. On the other hand, in this invention, since the diffusion prevention layer which consists of a ceramic ingredient without a catalyst component and reactivity has covered the ceramic carrier surface, a catalyst component does not diffuse it into the interior of a diffusion prevention layer, and also the ceramic honeycomb structure. Therefore, there is no fear of degradation of the catalyst performance degradation by diffusion and support, and the ceramic catalyst object which maintains the function over a long period of time can be realized. Moreover, a ceramic honeycomb structure object ingredient is not restricted, but since the ceramic ingredient containing a catalyst component and Si which is easy to react can also be used, if cordierite is used, the catalyst for emission gas purification which is excellent in thermal shock resistance with low cost will be acquired.

[0047]

[Example] The example and the example of a comparison for checking the effectiveness of this invention are shown below. As a cordierite-ized raw material, talc, the kaolin, the alumina, and the aluminum hydroxide were used, and the powder of these raw materials was prepared so that it might become near the point of cordierite forming [theoretical]. It is 100 micrometers of cell wall thickness about what carried out optimum dose addition and kneaded a binder, lubricant and a moisturizer, and moisture in this raw material. Extrusion molding was carried out to cel consistency 400cps (cel number per 1 square inch), and a honeycomb configuration with a diameter of 50mm. After heating this honeycomb structure object to 800 degrees C in the atmospheric-air ambient atmosphere and degreasing, it calcinated by holding at 1390 degrees C for 2 hours.

[0048] On the acquired honeycomb structure object, gamma-aluminum 2O₃, Y₂ O₃, and NiO, CuO and ZnO, La 2O₃ which is the oxide of a lanthanoids, CeO₂, Er 2O₃, and Yb 2O₃ It formed by the coat approach which shows the becoming diffusion prevention layer in Table 1, respectively, and the ceramic support which was able to be burned at 1000 degrees C was manufactured among atmospheric air (examples 1-9). Furthermore, before forming the diffusion prevention layer of examples 1-9, they are aluminum₂ TiO₅, ZnO, Y₂ O₃, AlN, aluminum 2O₃, and TiO₂. The ceramic support which formed by the coat approach which shows the becoming interlayer in Table 1, respectively, and formed the diffusion prevention layer similarly after that was manufactured (examples 10-18).

[0049] It was made easy to support by pretreatments (the chemical technique, the electrochemical

technique, etc.) beforehand on a honeycomb structure object, or that it is with an oxide method among the coat approaches adds mechanical actuation (ultrasonic rocking equipment, a vacuum pump, centrifugal separation machine, etc.), and it was made be a dip method using the DIP liquid prepared using the metallic-oxide particle, and to fill up homogeneity to a pore front face. There is a dip method using the DIP liquid which prepared the metal alkoxide as a start raw material with the alkoxide method. A spatter, vacuum evaporation, etc. are used for being with PVD. A metal target moreover, by oxygen gas flowing down The target of the oxide or a non-oxide by or the approach of forming membranes by the gas flowing down using at least one of the reducing gas, such as oxidation gas, such as inert gas, nitrogen, and oxygen, and hydrogen, according to the film (an ingredient, membraneous quality) to form There is the approach of introducing organic metal gas and forming membranes by the gas flowing down using at least one of the reducing gas, such as oxidation gas, such as inert gas, nitrogen, and oxygen, and hydrogen, according to the film (an ingredient, membraneous quality) to form, with a CVD method. In PVD and a CVD method, the film was formed in homogeneity by preparing temperature or a pressure gradient in the gas passageway of a honeycomb structure object thru/or equipment etc.

[0050] The thickness of the formed diffusion prevention layer and an interlayer was about 5 micrometers or less which is as being shown in Table 1 and is all the average pole diameter of a honeycomb structure object. In addition, each melting point of the oxide which constitutes a diffusion prevention layer and an interlayer was 1000 degrees C or more (1026 thru/or 2410 degrees C).

[0051] The potassium nitrate which contains the potassium as NOx occlusion material in the obtained ceramic support was applied, the coefficient of thermal expansion of the direction of passage when holding at 900 degrees C for 5 hours and the collapse reinforcement of the direction of passage were measured, respectively, and the result was described in Table 1. Here, measurement of a coefficient of thermal expansion was performed by the pusher bar type thermal-expansion meter method, and the coefficient of thermal expansion of the average between 25 degrees C and 800 degrees C estimated. The collapse reinforcement of the direction of passage of a honeycomb structure object cut down the cylinder with a die length of 1 inch for the diameter of 1 inch, and made collapse reinforcement the pressure at the time of adding a load in the direction of passage and being destroyed.

[0052]

[Table 1]

	拡散防止層			中間層			流路方向の 熱膨張係数 ($\times 10^{-6}/^{\circ}\text{C}$)	流路方向の 圧縮強度 (MPa)
	材料	コート 方法	膜厚 (μm)	材料	コート 方法	膜厚 (μm)		
実施例 1	$\gamma\text{-Al}_2\text{O}_3$	酸化物法	2.5	なし	—	—	1.2	10.5
実施例 2	Y_2O_3	アルコキシド法	1.5	なし	—	—	1.0	11.9
実施例 3	NiO	PVD 法	0.5	なし	—	—	1.2	11.5
実施例 4	CuO	酸化物法	2.0	なし	—	—	1.2	12.3
実施例 5	ZnO	CVD 法	0.7	なし	—	—	0.9	11.4
実施例 6	La_2O_3	アルコキシド法	1.7	なし	—	—	1.2	12.2
実施例 7	Ce_2O_3	酸化物法	3.5	なし	—	—	1.2	10.8
実施例 8	Er_2O_3	酸化物法	1.8	なし	—	—	1.2	11.3
実施例 9	Yb_2O_3	酸化物法	1.2	なし	—	—	1.1	11.0
実施例 10	$\gamma\text{-Al}_2\text{O}_3$	酸化物法	0.8	Al_2TiO_5	酸化物法	0.5	1.0	12.0
実施例 11	Y_2O_3	アルコキシド法	1.0	ZnO	酸化物法	0.5	0.9	12.8
実施例 12	NiO	PVD 法	0.5	Y_2O_3	酸化物法	0.5	1.0	12.0
実施例 13	CuO	酸化物法	1.5	ZnO	CVD 法	0.5	1.0	12.5
実施例 14	ZnO	CVD 法	0.7	Al_2TiO_5	酸化物法	0.5	0.8	12.2
実施例 15	La_2O_3	アルコキシド法	1.2	AlN	PVD 法	0.5	1.0	12.4
実施例 16	CeO_2	酸化物法	1.0	Al_2O_3	アルコキシド法	0.5	1.0	12.8
実施例 17	Er_2O_3	酸化物法	1.3	AlN	PVD 法	0.5	1.0	12.3
実施例 18	Yb_2O_3	酸化物法	1.2	TiO_2	PVD 法	0.5	0.9	13.0

[0053] Next, the ceramic support in which the diffusion prevention layer which becomes the cordierite honeycomb structure object acquired by the same approach as the above as an example of a comparison from ingredients other than this invention shown in Table 1, without forming a diffusion prevention layer was formed was manufactured (examples 1-8 of a comparison). Also about these ceramic support, the same trial was performed, the coefficient of thermal expansion of the direction of passage and the collapse reinforcement of the direction of passage were measured, and the result was described in Table 2. In the example 1 of a comparison which does not form a diffusion prevention layer, the coefficient of thermal expansion is high with $1.8 \times 10^{-6}/^{\circ}\text{C}$ so that clearly [Table 1 and Table 2]. Usually, the coefficient of thermal expansion of the cordierite honeycomb structure object itself is considered to be because for the potassium to have been spread and for the presentation to have changed into cordierite by heat-treating at an elevated temperature with about abbreviation $0.5 \times 10^{-6}/^{\circ}\text{C}$, since it is low. Moreover, it turns out that the collapse reinforcement of the direction of passage is also much less than 10MPa(s) needed for bearing the attachment load to a catalytic converter, and collapse reinforcement falls greatly by the reaction of cordierite and a potassium.

[0054]

[Table 2]

	拡散防止層			中間層			流路方向の 熱膨張係数 ($\times 10^{-6}/^{\circ}\text{C}$)	流路方向の 圧縮強度 (MPa)
	材料	コート 方法	膜厚 (μm)	材料	コート 方法	膜厚 (μm)		
比較例 1	なし	—	—	なし	—	—	1.8	4.6
比較例 2	$\alpha\text{-Al}_2\text{O}_3$ (コランダム)	酸化物法	2.0	なし	—	—	1.6	6.0
比較例 3	TiO_2	アルコキッド法	1.6	なし	—	—	1.7	5.1
比較例 4	ZrO_2	アルコキッド法	1.7	なし	—	—	1.6	6.5
比較例 5	CoO	酸化物法	2.5	なし	—	—	1.8	4.1
比較例 6	WO_3	PVD 法	0.8	なし	—	—	1.9	4.0
比較例 7	Fe_2O_3	酸化物法	3.0	なし	—	—	1.8	5.0
比較例 8	チタン酸 アルミニウム	酸化物法	6.0	なし	—	—	1.6	4.8

[0055] On the other hand, each ceramic support of examples 1-9 has practically the coefficient of thermal expansion of the direction of passage fully as low as less than $[1.5 \times 10^{-6}/^{\circ}\text{C}]$, and has satisfied 10MPa(s) by which the collapse reinforcement of the direction of passage is also needed for bearing the attachment load to a catalytic converter. Diffusion of a potassium is prevented by the diffusion prevention layer of examples 1-9, and this shows that the reaction of cordierite and a potassium has not arisen. Moreover, the ceramic support of the examples 10-18 in which the interlayer was formed had the still lower coefficient of thermal expansion of the direction of passage, collapse reinforcement is large and the improvement in the engine performance by the interlayer was checked.

[0056] Drawing 3 is CeO_2 chosen as a diffusion prevention layer of an example 6. It is the X diffraction chart which shows not having reactivity with a potassium. CeO_2 When each powder of a potassium nitrate is mixed, it heat-treats at 900 degrees C for 5 hours and the change heat treatment before (drawing Johan section) and after heat treatment (bottom half section of drawing) is investigated, it is before and after heat treatment, and it is CeO_2 . It is changeless at a peak and not reacting with a potassium was checked.

[0057] Moreover, as for the ceramic support in which the diffusion prevention layer of the examples 2-8 of a comparison was formed, it turns out that the coefficient of thermal expansion of the direction of passage is over $1.6 - 1.9 \times 10^{-6}/^{\circ}\text{C}$ and $1.5 \times 10^{-6}/^{\circ}\text{C}$, is [collapse reinforcement] much less than 4.0-6.5MPa and 10MPa(s), and the diffusion prevention effectiveness is not acquired with these ingredients. Drawing 4 and 5 are TiO_2 which constitutes the diffusion prevention layer of the examples 3 and 4 of a comparison, and ZrO_2 . It is the X diffraction chart which shows that it has reactivity with a potassium. The place which mixed with the powder of a potassium nitrate and was heat-treated at 900 degrees C for 5 hours, The peak of $\text{K}_2\text{Ti}_2\text{O}_5$ which is a resultant with a potassium, respectively, $\text{K}_2\text{Ti}_4\text{O}_7$ (drawing 4), and $\text{K}_2\text{Zr}_3\text{O}_7$ (drawing 5) was seen, and it was checked that TiO_2 and ZrO_2 react with a potassium.

[0058] In order to investigate the situation of diffusion of the potassium inside [after heat treatment] a honeycomb structure object about the ceramic support which formed the diffusion prevention layer (Y_2O_3 , NiO , and CeO_2) of examples 2, 3, and 7 in drawing 6, the result of having measured the potassium levels from the front face in contact with a potassium nitrate to a depth of 90 micrometers by EPMA is shown. In not forming a diffusion prevention layer, it becomes 15atm(s)% (a diffusion depth of 100 micrometers), but as shown in drawing, potassium levels are as low as less than [1atm%] to a depth of 90 micrometers, and it turns out that diffusion of a potassium can be prevented by the diffusion prevention layer.

[0059] To drawing 7, they are Y_2O_3 and CeO_2 . It uses, 49% of porosity, 31%, 22%, and 15% of pellet is produced, and the result of having investigated the situation of the diffusion of a potassium when carrying the powder of a potassium nitrate, respectively and heat-treating at 900 degrees C for 5 hours is shown. When the potassium levels from the front face in contact with a potassium nitrate to a depth of about 1mm are measured by EPMA about the pellet cross section after heat treatment, as shown in drawing, all of the potassium levels inside the pellet except a front face are as low as less than [1atm%] (limit of detection), and it turns out that diffusion of a potassium can be prevented.

[0060] To drawing 8, they are SiC and Si₃N₄ as a comparison ingredient. A pellet (46% of porosity) is produced and the result of having investigated the situation of the diffusion of a potassium when carrying the powder of a potassium nitrate and performing same heat treatment is shown. When the potassium levels from the front face in contact with a potassium nitrate to a depth of about 1mm are similarly measured by EPMA about the pellet cross section after heat treatment, as shown in drawing, it turns out that the potassium has diffused all to the interior of a pellet.

[0061] The thickness below the average pole diameter shows the relation of the coefficient of thermal expansion of the direction of passage of the glass thickness and ceramic support when forming an interlayer and a diffusion prevention layer to a cordierite honeycomb structure object at drawing 9. The thickness of a diffusion prevention layer (Y₂O₃) set to 0.3 micrometers and 0.6 micrometers, produced the ceramic support to which an interlayer's (ZnO) thickness was changed in 0.2-0.8 micrometers per the each, and measured the coefficient of thermal expansion of the direction of passage by the approach mentioned above. It is shown that the coefficient of thermal expansion is changing and the optimal thickness exists about each thickness of an interlayer and a diffusion prevention layer with the combination of the thickness of an interlayer (ZnO) and a diffusion prevention layer (Y₂O₃) as shown in drawing. Since a coefficient of thermal expansion and contraction change with each formation approach of an interlayer and a diffusion prevention layer, an ingredient, and particle size, this is predicted to be that from which an optimum value also differs according to those combination.

[0062] In case a diffusion prevention layer (Y₂O₃) is formed in drawing 10 with a dip method, it carries out to DIP liquid by repeating a series of processes dried [are immersed and] and calcinated two or more times, and the relation between the count of a repeat and the coefficient of thermal expansion of the direction of passage is shown in it. The inside of drawing, and Y₂O₃ B liquid which prepared O₃ A liquid using the metallic-oxide particle are the DIP liquid which prepared the metal alkoxide as a start raw material. The coefficient of thermal expansion of the direction of passage is decreasing, so that from this drawing and the count of a repeat increases, and it is predicted that it is the result of burying the very small crack produced in the process in which it results [from the immersion to the DIP liquid which is the 1st time] in baking by repeating with 2 times and 3 times. Thus, the effectiveness which controls diffusion can be heightened by adopting as DIP liquid the approach of repeating a series of processes dried [are immersed and] and calcinated two or more times.

[0063] In addition, although the above-mentioned example described only diffusion of the potassium as a catalyst component, even when other alkali metal or alkaline earth metal are made to support, it is checking that the same effectiveness is acquired. Moreover, it is checked also about SiC(s) other than cordierite, Si₃N₄, and a mullite as a honeycomb structure object that the same effectiveness is acquired.

[Translation done.]